

## EUROPIUM-DOPED GALLIUM-INDIUM OXIDES AS RED EMITTING ELECTROLUMINESCENT PHOSPHOR MATERIALS

### TECHNICAL FIELD

This invention relates to new phosphor materials exhibiting electroluminescence based on metal oxides and methods for their production. More particularly, the invention relates to new europium-doped gallium-indium oxide phosphors and use thereof as electroluminescent materials.

### BACKGROUND ART

Electroluminescence (EL) occurs by the emission of light from a phosphor in response to a sufficiently high electric field developed across the phosphor. Phosphor refers to those materials that emit light in response to the application of a field across the material. Thin film electroluminescent devices have a basic structure comprising a phosphor film or layer sandwiched between two electrodes.

A typical EL device 20 (shown in Fig. 1) consists of a glass substrate 22, a first electrode 24 consisting of a transparent conducting electrode such as indium tin oxide (ITO) deposited onto the glass substrate, and then a first insulating dielectric layer 26 deposited onto the ITO. The phosphor layer 28 is then deposited onto the first insulating dielectric layer 26 and then a second insulating dielectric layer 30 is deposited onto the phosphor layer, followed by a second electrode 32 of metal such as aluminum deposited onto the second insulating dielectric layer 30.

Application of an effective voltage across the two electrodes 24, 32 produces the electric field strength required to induce electroluminescence in the phosphor 28. The role of the dielectric layers 26, 30 is to avoid dielectric breakdown of the phosphor, and to form a suitable interface on either side of the phosphor layer. In some cases, including the results presented in this invention, one of the dielectric layers may be eliminated and EL emission still results.

There is strong commercial interest in achieving a wide spectral range in electroluminescent phosphors for visible display application and in particular for making color flat panel displays. Sulphide phosphor  $\text{ZnS:Mn}$  is a well known efficient light emitter in electroluminescence as discussed in T. Inoguchi, M. Takeda, Y. Kakihara, Y. Nakata, M. Yoshida, SID'74 Digest, p. 84-85, 1974. A significant drawback to this phosphor is that it is moisture sensitive and is prone to reacting with oxygen especially when electrically driven. Known electroluminescent materials being studied include materials such as  $\text{SrS:RE}$ , see W.A. Barrow, R.E. Coover, C.N. King, Digest 1984 SID International Symposium, Los Angeles, p. 249,  $\text{SrGa}_2\text{S}_4\text{:RE}$  and  $\text{CaGa}_2\text{S}_4\text{:RE}$  as disclosed in W.A. Barrow, R.C. Coover, E. Dickey, C.N. King, C. Laakso, S.S. Sun, R.T. Tuenge, R. Wentross, Digest 1993 SID International Symposium, Seattle, p. 761; G. Mueller (editor), Electroluminescence II. V 65, Semiconductors and Semimetals, Academic Press, San Diego, 2000, p. 143-145. While these materials do achieve red, green and blue emission, the gallium-based sulphides suffer from low brightness, difficulty of preparation and stability problems.

It has recently been demonstrated that in the gallate based family of materials,  $\text{ZnGa}_2\text{O}_4\text{:Mn}$  could achieve bright and stable electroluminescence, see T. Minami, S. Takata, Y. Kuroi, T. Maeno, Digest 1995 SID International Symposium, Orlando, p. 724; and T. Minami, Y. Kuroi, S. Takata, Display Phosphors Conference, San Diego, Nov. 13-16, 1995, p. 91. They obtained good green emission ( $200 \text{ cd/m}^2$  at 60 Hz at up to  $0.9 \text{ lm/W}$ ) but only obtained  $0.5 \text{ cd/m}^2$  blue, and  $11.0 \text{ cd/m}^2$  red at a drive frequency of 1000 Hz, which are not practical brightness values for a display by replacing Mn with Ce and Eu, respectively. They annealed these phosphor materials at  $1020^\circ\text{C}$  in argon.

More recently, Minami et al. have doped  $\text{ZnGa}_2\text{O}_4$  with chromium to generate a better red phosphor, claiming  $120 \text{ cd/m}^2$  at 1000 Hz, as disclosed in T. Minami, Y. Kuroi, S. Takata, T. Miyata, presented at Asia Display '95, Oct. 16-18, Hamamatsu. However it is not feasible to achieve full color in  $\text{ZnGa}_2\text{O}_4$  since rare earths are not compatible with this host lattice due to the size mismatch between Zn or Ga and the rare earth ions.

Recently it has been demonstrated that  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  could achieve electroluminescence, see T. Miyata, T. Minami, Y. Honda and S. Takata, SID '91 Digest, p. 286-289, 1991. Thin films were RF magnetron sputtered onto polished  $\text{BaTiO}_3$  substrates using the method disclosed in T. Minami, T. Miyata, S. Takata, I. Fukuda, SID'92 Digest, p. 162. A good brightness of  $200 \text{ cd/m}^2$  was achieved at 60 Hz with an efficiency of  $0.8 \text{ lm/W}$ . A drawback to these films is that they had to be annealed at  $1000^\circ\text{C}$  for several hours, which severely limits their applicability to practical substrates for displays.

In this group, new oxide phosphors based on doped gallium oxides, alkaline earth gallates and zinc germinates have been found exhibiting excellent electroluminescence. A series of alkaline earth gallates doped or co-doped with Eu and Tb exhibits red, bluish-green and white electroluminescence with promising brightness and efficiency, see United States Patent Nos. 5,897,812, and 5,788,882, 1998; and A.H. Kitai, T. Xiao, G. Liu, H. Li, SID '97 Digest, 1997, p. 419-422; and T. Xiao, A.H. Kitai, SID '97 Digest, 1997, p. 310-313. Bright green emission has been obtained from  $\text{Zn}_2\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_4$  doped with Mn. The maximum brightness and efficiency at 60 Hz drive are  $377 \text{ cd/m}^2$  and  $0.9 \text{ lm/W}$ , respectively, United States Patent No. 5,897,812.

Recent study showed that the red EL phosphor  $\text{Ga}_2\text{O}_3\text{:Eu}$  has the maximum brightness and efficiency of  $550 \text{ cd/m}^2$  and  $0.38 \text{ lm/W}$ , respectively, when driven at 60 Hz. It also exhibits long-term stability at brightness of  $840 \text{ cd/m}^2$  over 2500 hours at 370 V and 650 Hz on a ceramic substrate, see D. Stodilka, A.H. Kitai, Z. Huang, K. Cook, SID '00 Digest, 2000, p. 11-13.

This phosphor was also incorporated in an EL device using a glass substrate, where a maximum brightness of  $290 \text{ cd/m}^2$  at a drive voltage of 330 V at 60 Hz is achieved. The maximum efficiency is  $0.38 \text{ lm/W}$ , see A.H. Kitai, X. Deng, D.V. Stevanovic, Z. Jiang, S. Li, N. Peng, B.F. Collier, SID '02 Digest, 2002, p. 380-383.

A modified red phosphor was reported recently using  $\text{MgGa}_2\text{O}_4\text{:Eu}$ , which achieved a luminance of over  $450 \text{ cd/m}^2$  at a drive voltage of 300 V at 120 Hz. Maximum efficiency is  $0.924 \text{ lm/W}$ , see Y. Yano, T. Oike, K. Nagano, 2002, Int'l. Conf. On Science

and Technology of Emissive Displays and Lighting, Proceedings, Sept. 23-26, 2002, Ghent, Belgium, p. 225-230.

As mentioned above, a major drawback to known electroluminescent materials is the need for post fabrication high temperature annealing (in the vicinity of 1000°C) of the films to produce electroluminescent behavior. The need for high temperature treatment results in severe restrictions in the choice of substrates with only a limited number being available for use under these conditions. High temperature annealing also increases the difficulty of producing EL films rapidly on a large scale. Another limitation of many electroluminescent materials is that they are restricted to emitting at particular wavelengths or in a relatively narrow wavelength range, such as yellow ZnS:Mn or blue-green SrS:Ce which are not ideal for color displays that requires emission in the red, green and blue parts of the visible spectrum. Electroluminescent materials based on sulphides inherently suffer from chemical stability problems such as oxide formation (since oxides are generally thermodynamically more stable than sulphides) which changes the electronic properties of the material over time.

The classic EL phosphor, ZnS:Mn, is yellow and has a peak wavelength of 580 nm. However, while it may be filtered red and green, most of the light is lost because only 10% of the light is passed through the red and green filters. Similarly, a drawback of SrS:Ce, which is green-blue, is that only about 10% of the light is passed through a blue filter.

The red emitting Ga<sub>2</sub>O<sub>3</sub>:Eu phosphor requires a higher operating voltage compared to other EL phosphors. The drive voltage of 370 V mentioned in D. Stodilka, A.H. Kitai, Z. Huang and K. Cook, SID '00 Digest, 2000, p. 11-13 is substantially higher than desired. A voltage well below 300 V would be preferred. Due to its red emission and good efficiency, however, the Ga<sub>2</sub>O<sub>3</sub>:Eu is an attractive phosphor, which also possesses the advantage that annealing to temperatures of only 600°C is required.

It would therefore be very advantageous to provide new electroluminescent materials that exhibit lower voltage operation than Ga<sub>2</sub>O<sub>3</sub>:Eu but still provide red

emission with good efficiency, and permit processing at 600°C or lower temperatures.

It would also be advantageous to provide a method of producing new EL materials that are chemically stable and do not react appreciably with water or oxygen. Known color phosphors such as SrS:Ce and other sulphides are not stable in these respects.

It is an object of this invention to provide electroluminescent materials which exhibit electroluminescent behaviour over the red portion of the electromagnetic spectrum useful in color electroluminescent including, for example, flat panel displays.

## DISCLOSURE OF INVENTION

The invention provides new phosphor materials exhibiting electroluminescence based on europium doped gallium-indium oxide materials.

In a preferred embodiment, the invention provides a mixed metal oxide having a formula  $\text{Ga}_{2-x-y}\text{In}_x\text{Eu}_y\text{O}_3$  wherein x spans the range 0.1 to 0.4 and y spans the range in which it is soluble in the phosphor.

In another aspect of the present invention, any of these electroluminescent phosphors may be used to provide an electroluminescent display device 20, having:

- a) a dielectric layer 30 having a front surface, a back surface and a conducting electrode 32 on the back surface thereof;
- b) an electroluminescent phosphor film 28 of any of the above-mentioned phosphor materials on said front surface; and
- c) a substantially transparent electrode 24 formed adjacent to said electroluminescent phosphor 28.

## DESCRIPTION OF DRAWINGS

Preferred embodiments of the invention will now be described, by way of example only, with reference to the drawings, in which:

Fig. 1 is a schematic sectional view of the structure of an electroluminescent device using a glass substrate;

Fig. 2 is a typical plot of emitted light intensity versus wavelength showing the electroluminescent spectrum of  $\text{Ga}_{2-x-y}\text{In}_x\text{Eu}_y\text{O}_3$  family of phosphors

Fig. 3 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.83}\text{Eu}_{0.17}\text{O}_3$  grown at 450°C, annealed at 600°C;

Fig. 4 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.83}\text{Eu}_{0.17}\text{O}_3$  grown at 500°C, annealed at 600°C;

Fig. 5 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$  grown at 450°C, annealed at 600°C;

Fig. 6 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$  grown at 500°C, annealed at 600°C;

Fig. 7 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$  grown at 540°C, annealed at 600°C;

Fig. 8 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.63}\text{In}_{0.2}\text{Eu}_{0.17}\text{O}_3$  grown at 500°C, annealed at 600°C; and

Fig. 9 are plots of brightness (left most vertical axis) and efficiency (right most vertical axis) versus voltage at 60 Hz of  $\text{Ga}_{1.43}\text{In}_{0.4}\text{Eu}_{0.17}\text{O}_3$  grown at 500°C, annealed at 600°C.

BEST MODE FOR CARRYING OUT THE INVENTION

As used herein, the term phosphor(s) refers to mixed metal oxides which exhibit electroluminescence (EL) when a suitable electric field is applied across the material. The various metal elements used in the production of the new oxide based materials exhibiting EL disclosed herein include gallium (Ga), europium (Eu) and indium (In).

## EXPERIMENTAL TECHNIQUES

A number of experimental electroluminescent (EL) devices of the kind generally shown in Fig. 1 were constructed in accordance with the invention in which the first insulating dielectric layer 26 was omitted. For ease of reference, the layers of the EL devices constructed are identified by the reference numerals used in Fig. 1.

The phosphor layers 28 used to demonstrate the invention were prepared by mixing commercial powder high purity  $\text{Ga}_2\text{O}_3$  (99.99921%) (from Eagle Picher),  $\text{Eu}_2\text{O}_3$  (99.99%) and  $\text{In}_2\text{O}_3$  (99.995%) (from Alfa-Aesar), in the appropriate ratios, and then firing the mixtures at 1100°C in air for 6-10 hours. The phosphor powders were then ground and pressed into 2-inch targets. A 2-inch RF magnetron gun was used to sputter a thin film phosphor layer 28 onto substrates. Substrates 22 used in this invention were glass (Corning type 1737) of thickness 1.1 mm which had a first electrode 24 comprising a transparent indium-tin oxide coating of 0.3 micron onto which the thin film phosphor 28 was sputtered.

The indium-tin oxide coated substrate 22 was mounted onto a rotating holder located above the gun and heated to 450-540°C with a substrate heater. The sputtering process was carried out at a pressure of 20 mtorr, consisting of 30% to 45%  $\text{O}_2$  in Ar. The thickness of the deposited films 28 was in the range of 2000 and 5000 Å. The films 28 were annealed in air at 600°C for 1 hour. A 2 micron thick strontium titanate dielectric layer 30 was deposited on top of the phosphor layer 28. Growth was carried out in three stages. The first 0.9 micron was sputtered by RF sputtering. The second 0.2 micron was grown by sol-gel. The final 0.9 micron was again sputtered by RF sputtering.

Finally, aluminum (Al) was evaporated as a top electrode 32 to a thickness of

about 1000 Å.

EL emission spectra were taken using an Ocean Optics S-2000 spectrometer and the color coordinates were obtained using OOIColor Excel Template (Ocean Optics, Inc.). Brightness of the EL devices was measured with a Minolta Luminance Meter LS-100. Efficiency was obtained by the Sawyer-Tower method.

## RESULTS

The phosphors 28 studied herein showed bright electroluminescence (EL) with red color. The spectrum shown in Fig. 2 is representative of all the EL results for the phosphor system  $\text{Ga}_{2-x-y}\text{In}_x\text{Eu}_y\text{O}_3$  and almost no dependence on the value of  $x$  was observed. The typical CIE colour coordinates of the red emission was measured as  $a = 0.64$  and  $b = 0.36$ .

Fig. 3 shows the measured brightness and efficiency versus voltage of a reference device with phosphor composition of  $\text{Ga}_{1.83}\text{Eu}_{0.17}\text{O}_3$ . The growth temperature of the phosphor layer was 450°C and the anneal temperature was 600°C. Maximum efficiency was 0.38 lm/W at a drive voltage of 260 V. Phosphor thickness is about 0.27 µm.

Fig. 4 shows that for another reference device with phosphor composition of  $\text{Ga}_{1.83}\text{Eu}_{0.17}\text{O}_3$ , a growth temperature of 500°C and an anneal temperature of 600°C, the maximum efficiency was 0.28 lm/W at a drive voltage of 210 V. Phosphor thickness is about 0.23 µm.

The rather high drive voltages required are illustrated by Figs. 3 and 4. In spite of a thinner phosphor layer used in Fig. 4, of only 0.23 µm, a drive voltage of 210 V is required for maximum efficiency.

Fig. 5 shows that for a device with phosphor composition  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$ , a growth temperature of 450°C and an anneal temperature of 600°C, the maximum efficiency was 0.36 lm/W at a drive voltage of 230 V. Phosphor thickness is about 0.315 µm.

Fig. 6 shows that for a device with phosphor composition  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$ , a



growth temperature of 500°C and an anneal temperature of 600°C, the maximum efficiency was 0.32 lm/W at a drive voltage of 250 V. Phosphor thickness was 0.42  $\mu\text{m}$ .

Fig. 7 shows that for a device with phosphor composition  $\text{Ga}_{1.73}\text{In}_{0.1}\text{Eu}_{0.17}\text{O}_3$ , a growth temperature of 540°C and an anneal temperature of 600°C, the maximum efficiency was 0.32 lm/W at a drive voltage of 195 V. The phosphor thickness was about 0.255  $\mu\text{m}$ .

Fig. 8 shows that for a device with phosphor composition  $\text{Ga}_{1.63}\text{In}_{0.2}\text{Eu}_{0.17}\text{O}_3$ , a growth temperature of 500°C and an anneal temperature of 600°C, the maximum efficiency was 0.31 lm/W at a drive voltage of 200 V. The phosphor thickness was 0.37  $\mu\text{m}$ .

Finally, Fig. 9 shows that for a device with phosphor composition  $\text{Ga}_{1.43}\text{In}_{0.4}\text{Eu}_{0.17}\text{O}_3$ , a growth temperature of 500°C and an anneal temperature of 600°C, the maximum efficiency was 0.175 lm/W at a drive voltage of 180 V. The phosphor thickness was about 0.32  $\mu\text{m}$ .

It is clear from examination of Figs. 3, 4, 5, 6, 7, 8 and 9, that a trend toward lower operating voltages is present. Since the operating voltage also depends on phosphor layer thickness, however, the trend is not as clear as if all the devices were grown using the same phosphor thickness. This was not feasible due to the limitations of our experimental technique, which provides only approximate thickness control.

The difficulty may be overcome by calculating the threshold electric field in the phosphor layer necessary to achieve luminescence in each device. The calculation of electric field compensates for the phosphor layer thickness. For Figs. 3 and 4, the threshold electric field is about  $4.27 \times 10^8$  V/m. For Figs. 5, 6 and 7, the threshold electric field is about  $3.97 \times 10^8$  V/m. For Fig. 8, the threshold electric field is  $3.4 \times 10^8$  V/m. For Fig. 9, the threshold electric field is  $3.26 \times 10^8$  V/m.

Now the trend is clearer. Results from more samples grown under similar conditions confirm the decrease in electric field, showing a ~25% decrease in electric

field on samples of composition  $\text{Ga}_{1.43}\text{In}_{0.4}\text{Eu}_{0.17}\text{O}_3$  compared with samples of composition  $\text{Ga}_{1.83}\text{Eu}_{0.17}\text{O}_3$ .

#### INDUSTRIAL APPLICABILITY

Benefits of a lower electric field include lower drive voltages and lower electrical stress on the insulating layer in the EL device. It is well known to those familiar with EL devices that the insulating layer is subjected to electric fields that depend on the electric field applied to the phosphor. If the electric field in the insulator layer is reduced, better drive reliability is obtained.

In addition, the EL device exhibits electrical capacitance. If the electric field necessary for EL operation is decreased in the phosphor layer, then phosphor layer thickness may be increased, and the capacitance of the EL device will decrease. It is generally desirable to have as small a device capacitance as possible, which reduces the electric current and power dissipation in EL display devices.

It will be appreciated that while the fabrication of the new electroluminescent phosphors disclosed herein has been described using sputtering as the film preparation method, other methods known to those skilled in the art may be used. Other methods of fabrication include electron beam deposition, laser ablation, chemical vapor deposition, vacuum evaporation, molecular beam epitaxy, sol gel deposition and plasma enhanced vacuum evaporation to mention a few.

Various thin film dielectrics 26, 30 used in electroluminescent applications include  $\text{SiO}_2$ ,  $\text{SiON}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaTiO}_3$ ,  $\text{BaTa}_2\text{O}_6$ ,  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{PbNb}_2\text{O}_6$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ - $\text{TiO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiAlON}$ . Dielectrics which may be used as an insulator in the present invention may be selected from the above list and deposited onto glass, silicon or quartz substrates 22, to mention just a few.

While the results disclosed herein were obtained using thin film dielectrics 26, 30 thick films on ceramic or glass substrates 22 may also be used. The ceramic substrate

22 may be alumina ( $\text{Al}_2\text{O}_3$ ) or made from the same ceramic as the thick film itself. Thick dielectric films of  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{PbTiO}_3$ , to mention just a few, may be used.

Variations of the EL laminate device 20 configuration will be readily apparent to those skilled in the art. Such variations will in part be dependent on the intended commercial use of the EL device. Where the EL device is a flat panel display, the substrate 22 is made of glass and the associated electrode layer 24 must be transparent or nearly so. By making the electrode layer 24 very thin, near transparency is achieved using materials such as the indium-tin oxide ITO of the above-described examples. An alternative material for use as a transparent electrode material would be a thin layer of ZnO:Al (aluminum doped zinc oxide). Alternatively, an alumina substrate 22 may be used onto which the lower conductive electrode 24 is deposited followed by a high dielectric constant material 26, a phosphor 28 and then an outer transparent electrode 32. Alternatively, a conductive electrode contact 24 may be deposited onto a glass or quartz substrate 22 followed by a dielectric layer 26, a phosphor 28, another dielectric layer 30 and a second electrode 32.

The EL characteristics of the phosphors may vary within the solubility range of the dopant(s) in the host lattice. Electronic interactions between dopant ions can play a role in determining the preferred concentration of dopant ions for maximum brightness and efficiency. This phenomenon, known as concentration quenching, results in decreasing brightness and efficiency for doping concentrations beyond a certain point within the solubility limit such that there will be preferred dopant concentrations which give optimum EL properties. The dopant content may therefore vary within its solubility range in the host lattice.

It is to be understood that the nomenclature or notation used herein to identify the new phosphor materials is not to be interpreted as limiting. For example, it is not necessarily the case that the Eu rare earth dopant substitutes for Ga in the host lattice of the gallates or for Ga and In in the gallium-indium oxides. It will also be appreciated by those skilled in the art that the allowable ranges of concentration of dopants in the

different new phosphor materials disclosed herein will depend in part on the solubility limit of the dopant in the oxides.

It is also to be understood that deviations in the cation concentrations in the phosphors may occur due to the sputtering process. These deviations in stoichiometry may have influence on the resulting EL behaviour; however, the validity of results presented herein is not compromised by such deviations.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments that would be obvious to those skilled in the art.

LIST OF REFERENCE NUMERALS

- 20 EL device
- 22 glass substrate
- 24 1<sup>st</sup> electrode
- 26 dielectric layer
- 28 phosphor layer
- 30 2<sup>nd</sup> dielectric layer
- 32 2<sup>nd</sup> electrode